

# The Determination of Pore Structure in Graphites from Low Pressure Gas Flow Measurements

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## Introduction

It is essential to determine the pore structure in polygranular graphites in order to understand and predict structure-related properties, such as strength and corrosion resistance, and hence to assess the utility and performance of these materials for different applications, for example in the nuclear power industry. Model pore structure parameters in graphites and other porous media may be determined from measurements of gas transport properties. The mechanism of gas transport is governed largely by the ratio of (i) the number of gas phase inter-molecular collisions in the pores to (ii) molecule-pore wall collisions. This ratio is proportional to the ratio of the molecular mean free path and the pore size. The mean free path is inversely proportional to total pressure and previous analyses of gas transport properties in graphites<sup>1</sup> have been confined to high pressures (~ 100 kPa) where the effects of molecule-pore wall collisions can be neglected (i.e. molecular diffusion and permeation occur). In our earlier paper<sup>2</sup>, low pressure (< 15 kPa) helium-argon diffusion data were reported for three macroporous, polygranular graphites. It was concluded tentatively that molecule-pore wall collisions were dominant (i.e. Knudsen diffusion occurred). This paper presents a new analysis of similar results, and gives estimates of model gas transport pore structure parameters for the case where both collision types are important (i.e. transition diffusion).

## Experimental

A Wicke-Kallenbach apparatus described before<sup>2</sup> was used to measure the counter-diffusion of He and Ar through three isotropic polygranular graphites. The graphites are nuclear grades. Isobaric flows were determined at ambient temperatures and at total pressures between 0.1 and 15 kPa. Mole fraction gradients across the sample were maintained constant at unity.

## Analysis

An effective gas transport diffusivity in isotropic porous media may be defined as

$$D_i = J_i R T L / A P \Delta x_i \quad (1)$$

where  $J_i$  is the molar flow rate of gas  $i$  through a sample of length  $L$  parallel to flow and area  $A$  normal to flow,  $R$  is the gas constant,  $T$  is

the absolute temperature,  $P$  is the total pressure and  $\Delta x_i$  is the mole fraction difference for  $i$  across  $L$  (for this work  $\Delta x_i = 1$ ).

On the basis of a tortuous cylindrical capillary model for the gas transport pores in isotropic graphites<sup>3</sup>,  $D_i$  may be determined from simple molecular collision dynamics as a function only of  $P$ ,

$$D_i = \frac{1}{\tau_{\min}} \int_{\tau_{\min}}^{\tau_{\max}} K_i(P, r) U(r) dr \quad (2)$$

Equation (2) is a homogeneous Fredholm equation; the kernel is a function only of  $P$  and of transport capillary radius  $r$ ,

$$K_i(P, r) = (a_i r^2 / P) \ln[(b_i P r + 1) / (c_i P r + 1)], \quad (3)$$

where  $a_i$ ,  $b_i$  and  $c_i$  are known constants. The pore structure function is given by

$$U(r) = N_T P_T(r) / q \quad (4)$$

where  $N_T$  is the number density of transport capillaries,  $P_T(r)$  is the distribution function of  $r$ , and  $q$  is a geometric tortuosity factor.

Values for  $D_i$  are determined experimentally from (1). The problem is to estimate  $U(r)$  from (2). A least squares solution is unstable<sup>3</sup>. An estimate of  $U(r)$  can be furnished by the method of regularisation employed with a non-negativity constraint for  $P_T(r)$ <sup>3</sup>. The deconvoluted curve may then be normalised to unity to give a value for  $N_T/q$  and to give a distribution curve  $P_T(r)$ .

Limiting forms of (2) are well known at high and low pressure<sup>1,2</sup>. Regularisation is applicable only to the case of transition diffusion.

## Results and Discussion

The graphites used are summarised in Table 1. Figure 1 shows mean curves of the effective diffusivities for He and Ar. The two curves for each graphite show that coefficients are constant at low pressures and decrease for higher pressures. From (2) this indicates flow passing from pure Knudsen diffusion to transition diffusion. The onset of transition diffusion occurs at decreasing pressure for graphites of nominally increasing mean pore entrance diameter;

Table 1. Summary of Pore Structure and Gas Transport Properties.

Graphite	Mean P.E.D. ( $\mu\text{m}$ )	Pore Volume (%)		High Pressure ( $\approx 100$ kPa) Gas Transport Parameters		
		Open	Closed	Diffusivity Ratio ( $/10^{-3}$ )	Permeability Coefficients Viscous ( $/10^{-8} \text{ m}^2$ )	Slip ( $/10^{-8} \text{ m}$ )
A moulded	0.75	17.4	3.0	10.9	0.23	1.54
B isostatic pressed	2.4	8.6	7.6	2.4	0.15	0.60
C moulded	7.5	14.3	5.0	3.0	2.70	3.27

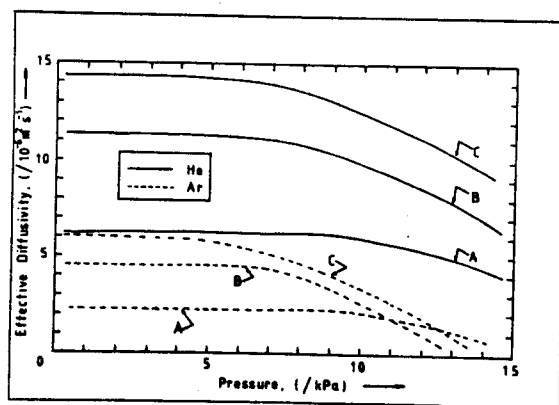


Figure 1. Effective diffusivity versus pressure.

this is consistent with mean free path arguments. For each graphite the ratio  $D_{\text{He}}/D_{\text{Ar}}$  appears constant with a mean of  $2.92 \pm 0.31$ , cf. the theoretical value of  $\sqrt{10} = 3.16$ , being the root of the ratio of molecular weights for Ar and He. In the range of experimental pressures, molecular diffusion does not occur since the diffusivities do not obey a reciprocal relation with pressure as would be expected for this regime from (2).

Estimated gas transport pore structure factors are summarised in Table 2. Distribution curves for pore radii are in Figure 2. Mean radii determined for graphites A, B and C from the regularised curves are  $0.45 \mu\text{m}$ ,  $1.32 \mu\text{m}$  and  $3.98 \mu\text{m}$  respectively; full-width-half-maximum values are  $0.24 \mu\text{m}$ ,  $0.57 \mu\text{m}$  and  $1.29 \mu\text{m}$ . These figures compare well with mean pore entrance diameters (P.E.D.s) from mercury porosimetry. Values for  $N_T$  and  $q$  agree well with those calculated from molecular diffusivity and permeability data ( $P \approx 100$  kPa). Density curves from regularisation are similar to those from Hg porosimetry; thus it appears that gas transport is governed by constrictions in the pores since it is well known that porosimetry is similarly constrained. Analysis suggests  $\approx 10\%$  of the open porosity is involved in gas transport.

Table 2. Estimated Gas Transport Pore Structure Parameters.

Graphite	High Pressure Work ( $\approx 100$ kPa)			This Work ( $< 15$ kPa)
	$N_T$ ( $/10^8 \text{ m}^{-3}$ )	$q$ (dimensionless)	$N_T/q$ ( $/10^8 \text{ m}^{-3}$ )	$N_T/q$ ( $/10^8 \text{ m}^{-3}$ )
A	3.2	9.7	3.3	2.7
B	0.35	6.8	0.51	0.42
C	0.17	4.2	0.40	0.33

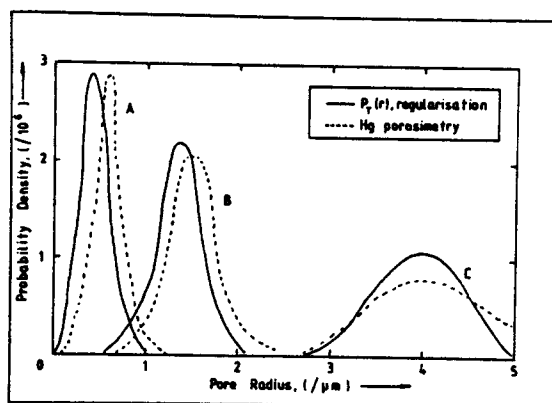


Figure 2. Pore radius distribution curves.

### Conclusion

A new method has been developed to estimate independently transport pore structure parameters in isotropic polygranular graphites. The method involves analysing the variation of effective binary gas diffusivity with pressure in the transition regime between pure Knudsen diffusion and pure molecular diffusion.

### Acknowledgement

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### References

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